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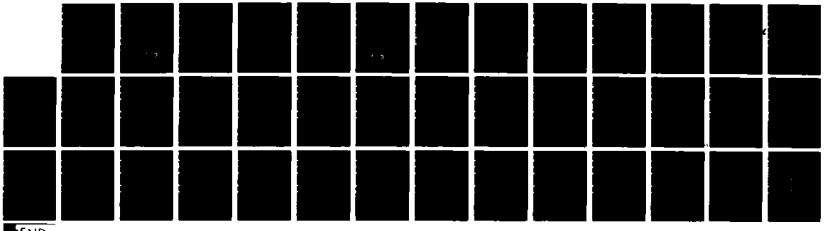

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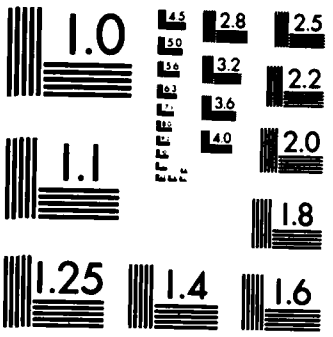

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EFFECT OF INTEGRATION TIME ON PRECISION OF ABSORBANCES MEASURED WITH A DIODE ARRAY UV-VIS SPECTROPHOTOMETER

AD-A146 952

by Joseph W. Hovanec
Reginald P. Seiders
J. Richard Ward

RESEARCH DIVISION

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Ultraviolet-visible spectrometry	Cobalt tetrasulfonated phthalocyanine
Statistics	Diode array spectrophotometer
Bartlett's test	Ultraviolet/visible light absorption
HP8450A	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Modern UV-VIS spectrophotometers such as the HP8450A equipped with a diode array controlled by a minicomputer can scan a spectrum from 200 to 800 nm in one second, or the instrument can time-average scans over a period of time denoted the "integration time." In order to see whether the precision was significantly enhanced by time-averaging, replicate measurements were made with holmium oxide, and a dyestuff with peak absorbance near unity, as well as a diluted sample of the dye with peak absorbance near 0.01 absorbance unit.

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20. Abstract (continued)

Measurements were made at 1-, 2-, 5-, 10-, 20-, and 40-second integration times. Bartlett's chi-squared statistic was used to test whether the variances were significantly different. The results showed that the variances were independent of integration time for all samples tested. The sample standard deviation was 0.001 absorbance unit for samples with peak absorbances near 1.0. For the diluted dye, the sample standard deviation was 2×10^{-4} absorbance unit.

PREFACE

This work was performed under Project 1L161101A71A, Research in Defense Systems, Scientific Area B during FY83.

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EFFECT OF INTEGRATION TIME ON PRECISION OF ABSORBANCES MEASURED WITH A DIODE ARRAY UV-VIS SPECTROPHOTOMETER

1. INTRODUCTION

Ultraviolet and visible-light absorption spectrometry has radically changed through the combination of multichannel detector technology with microcomputers. The new diode-array rapid-scan spectrophotometers can scan from 200 to 800 nm in less than a second. The rapid-scan feature opens the way for UV-VIS spectrophotometers as liquid-chromatography detectors and for high-production chemical analyses and also expands the capability in such traditional roles as monitoring kinetics, where one can now follow changes in the entire spectrum rather than one wavelength. Haas and coworkers described one early version of the diode-array spectrophotometer along with the merits of the various detector materials.[1] Later, Thomas[2] described the functioning and specifications of the Hewlett-Packard HP8450A diode-array spectrophotometer, with emphasis on multicomponent analysis using the software attendant to the HP8450A. Most recently, James[3] described the use of the HP8450A for multicomponent analysis of metals using 6M HCl as a nonspecific chromogenic agent.

In addition to rapid scanning, diode-array spectrophotometers can time average scans over a preset time, denoted the integration time. The question arises whether precision is enhanced significantly by time averaging, or conversely, what penalty is paid in situations where spectra cannot be averaged. To this end, we made replicate absorbance measurements at various integration times with the HP8450A diode-array spectrophotometer, using holmium oxide and a dyestuff (cobalt tetrasulfonated phthalocyanine (CoTSPC)) at two concentrations. In addition, the variances measured with replicate determinations were compared with the variances computed with a propagation-of-error analysis by the microcomputer integral to the HP8450A.

A similar analysis to determine the practical precision limits for inductively coupled plasma spectrophotometers has recently appeared,[4] in which the advantages were extolled of using replicate measurements to determine variance vs. propagation-of-error analysis.

2. EXPERIMENTAL

Absorbances were measured with the Hewlett-Packard HP8450A diode-array spectrophotometer equipped with an HP7470A plotter and an HP89100A temperature controller. Absorbances at given wavelengths were printed on an HP2621P printer through the RS232C port on the spectrophotometer.

The holmium oxide sample was supplied with the HP8450A. The CoTSPC dyestuff was prepared by a standard procedure.[5] Absorbances were measured in a 1-cm cell thermostatted at 25.0° C to preclude changes in absorbance through aggregation.[6] A stock solution of CoTSPC was prepared by dissolving the dyestuff in deionized distilled water to give a solution with peak absorbance near unity. Approximately 1 ml of this solution was diluted in a 100-ml volumetric flask to give a "diluted" solution with peak absorbance near 0.01 absorbance unit.

A more complete description of the theory of measurement by the HP8450A is provided in the appendix.

Barlett's chi^{2*} statistic[7] was used to test the null hypothesis that the variances from measurements at various integration times were equal. The test statistic for k samples with variance S_i^2 (i = 1,2...k) is

$$\chi^{2*} = \left\{ \frac{1}{1 + \frac{\sum_{i=1}^{k} \left(\frac{1}{\nu_i}\right) - \frac{1}{\nu}}{3(k-1)}} \right\} \cdot \left[\nu \ln S_p^2 - \sum_{i=1}^{k} \nu_i \ln S_i^2 \right] \qquad (1)$$

where S_i^2 = variance of i,

ν_i = degrees of freedom of sample i,

$\nu = \sum_i \nu_i$, and

$S_p^2 = \nu^{-1} \cdot \sum_i \nu_i^2 S_i^2$

If the null hypothesis is true, then χ^{2*} is approximately distributed as χ^2 with k-1 degrees of freedom. The null hypothesis is rejected if χ^{2*} is too large, so that this is a one-sided test. Table 1 lists the χ^2 distribution for 4 and 5 degrees of freedom at various probabilities.[8]

Table 1. The Chi-Square Distribution for Four and Five Degrees of Freedom

Probability	χ^{2*} ν = 4	χ^{2*} ν = 5
0.005	0.207	0.412
.001	.297	.554
.025	.484	.832
.05	.711	1.15
.10	1.06	1.61
.90	7.78	9.24
.95	9.49	11.07
.975	11.14	12.83
.990	13.28	15.09
.995	14.86	16.75

3. RESULTS AND DISCUSSION

3.1 Holmium Oxide.

Figure 1 illustrates the absorbance of holmium oxide vs. wavelength from 300 to 800 nm. Absorbances at two peaks, 361 nm and 444 nm, were used for subsequent analyses.

Three sets of experiments were performed with holmium oxide as follows: (a) absorbance and standard deviation as computed by microcomputer were measured at integration times of 1, 5, 10, 20, and 60 seconds; (b) at each integration time, 11 replicate absorbance measurements were made, from which a mean and standard deviation were calculated; and (c) absorbances were

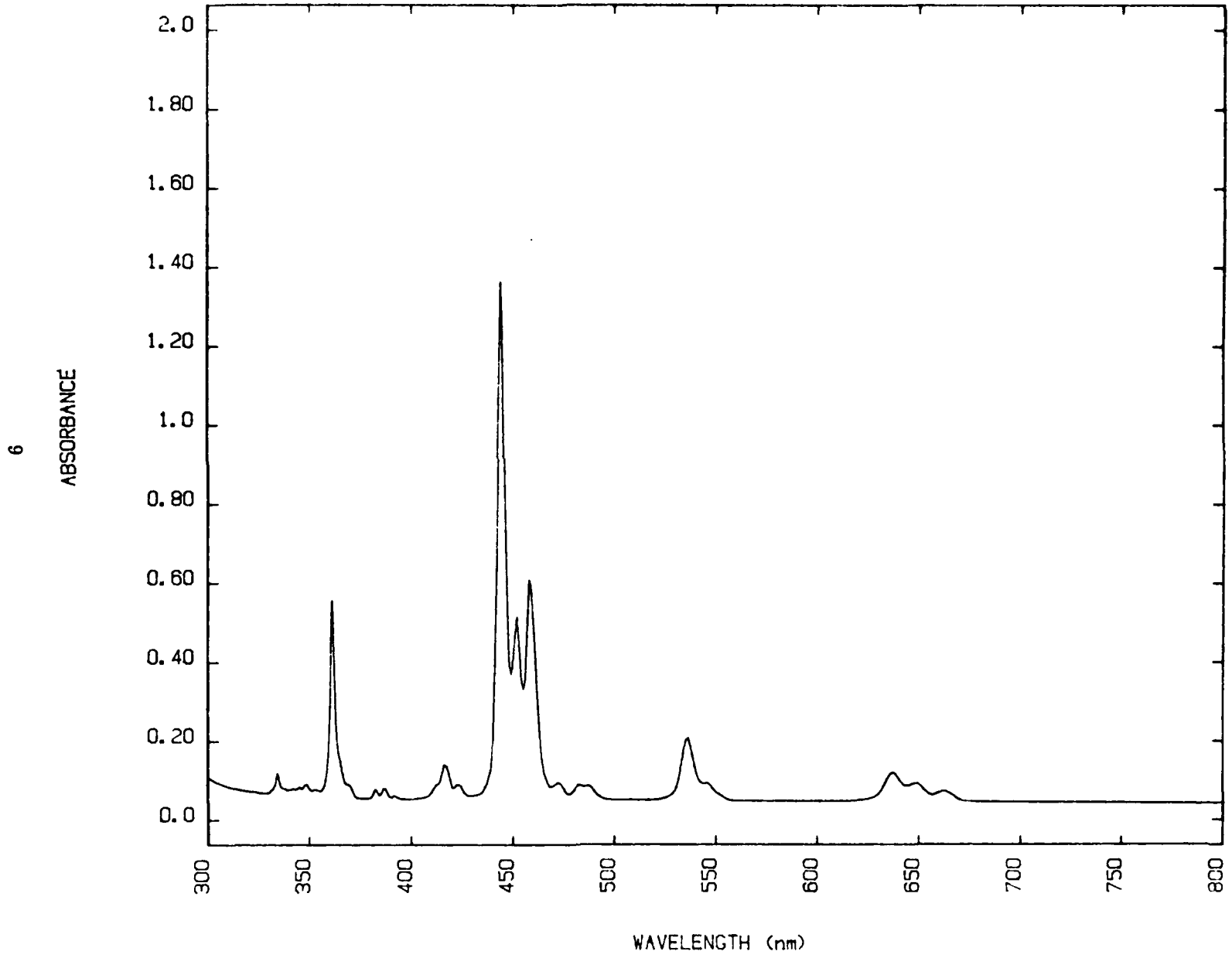

Figure 1. Absorbance of Holmium Oxide Versus Wavelength

measured for each integration time, then the holmium oxide was removed, the HP8450A was rebalanced, and the absorbances measured again at each integration time. This procedure was repeated four times, after which the mean and standard deviation were computed for each integration time. Then a two-way analysis of variance (ANOVA) was run to test whether removal and replacement of the holmium oxide introduced error.

The results of the measurements referred to above are listed in tables 2 through 5 along with the χ^{2*} statistic for the variances. From table 1 for four degrees of freedom, one can see that all the χ^{2*} are less than the value of χ^2 at the 95% confidence level (9.49). Hence, the null hypothesis that the variances for each integration time are the same is accepted.

Tables 6 and 7 present the ANOVA for the absorbances measured at 361 nm and 444 nm, respectively. The F-ratio for replacing the holmium oxide and rebalancing is significant at the 99% level, so one concludes that a significant error has been introduced. Such an error is a more realistic estimate of the instrument error when one is comparing spectra measured and stored on different days.

Table 2. Absorbance of Holmium Oxide at Various Integration Times; Error Calculated by Microcomputer in HP8450A

Integration Times	Absorbance x 361 nm mean	Absorbance x 361 nm std dev x 10^4	Absorbance 444 nm mean	Absorbance 444 nm std dev x 10^4
1	0.5648	±2.7	1.375	±2.7
5	5645	±1.4	1.374	±4.9
10	5645	±1.1	1.374	±4.9
20	5646	±0.97	1.375	±4.6
60	5649	±1.1	1.374	±4.9
χ^{2*} statistic[a]		5.1		0.65

[a]Degrees of freedom for each integration time computed on the basis of two measurements each second, so that for a given integration time, t, v in square (1) is (2t-1).

Table 3. Mean Absorbance for Eleven Scans of Holmium Oxide at Various Integration Times

Integration Times	Absorbance			
	361 nm		444 nm	
	mean	std dev x 10^4	mean	std dev x 10^4
1	0.5653	1.6	1.376	5.9
5	5652	1.9	1.376	9.1
10	5653	1.7	1.375	7.6
20	5654	2.0	1.375	6.6
60	5656	1.9	1.375	7.3
χ^{2*} statistic		0.64		5.5

Table 4. Effect of Rebalancing on Holmium Oxide Spectrum at 361 nm at Various Integration Times

Integration Times	Absorbance					
	I	II	III	IV	Mean	Std Dev x 10^4
1	0.5679	0.5678	0.5690	0.5694	0.5688	6.4
5	.5671	.5682	.5689	.5694	.5684	10.0
10	.5670	.5685	.5687	.5693	.5684	9.8
30	.5670	.5684	.5689	.5694	.5684	10.3
60	.5673	.5686	.5690	.5696	.5686	9.7
χ^{2*}						0.72

Table 5. Effect of Rebalancing on Holmium Oxide Spectrum at 444 nm at Various Integration Times

Integration Times	Absorbance					
	I	II	III	IV	Mean	Std Dev x 10^3
1	1.375	1.375	1.375	1.375	1.375	---
5	1.373	1.373	1.373	1.375	1.374	1.0
10	1.374	1.373	1.375	1.375	1.374	0.98
30	1.373	1.374	1.374	1.375	1.374	0.82
60	1.373	1.374	1.375	1.375	1.374	0.98
χ^{2*}						0.19

Table 6. Two-Way ANOVA Table for Holmium Oxide, λ = 361 nm

Source	TSS	Variance	df	F-Ratio
Rebalance	1271[a]	423.9	3	129[b]
Integration time	43.30	10.8	4	3.3
Residual	39.50	3.3	12	
Total	1354.55	71.3		

[a]Numbers coded by absorbance x 10^4 - 5600.

[b]Significant at 99% level (F(3,12) = 5.95)

Table 7. Two-Way ANOVA for Holmium Oxide, λ = 444 nm[a]

Source	TSS	Variance	df	F-Ratio
Rebalance	6.00	2.00	3	5.3[b]
Integration time	4.70	1.18	4	3.1
Residual	4.50	0.38	12	
Total	15.20			

[a]Numbers coded by absorbance x 10^3 - 1300.

[b]Significant at 95% level (F(3,12) = 3.49).

Table 8 compares the variances computed with the microcomputer with the variances from replicate measurements including the residual values from the ANOVA table. Because the replicate and residual variances are equivalent, self-consistency in the experiments is confirmed, and the variance computed by the microcomputer underestimates the variance determined from replicate runs.

Table 8. Comparison of Variances for Holmium Oxide Measurements

	λ = 361 nm		λ = 444 nm	
Source	Std Dev x 10^4	Variance x 10^8	Std Dev x 10^4	Variance x 10^8
Microcomputer[a]	1.5	2.2	4.4	19.4
Replicates	1.8	3.3	7.1	50.4
Residual	1.8	3.3	6.2	30.8

[a]Mean value of the variances computed by the microcomputer at each integration time.

3.2 CoTSPC Solution.

Figure 2 illustrates the absorption spectrum of a 1.97×10^{-5} M solution of CoTSPC in water at 25° C, hereafter referred to as the CoTSPC solution as compared with later reference to the "diluted" CoTSPC solution. Absorbances were measured at three peaks, 214, 321, and 660 nm. In the first set of runs, the absorbances were measured at integration times of 1, 2, 5, 10, 20, and 40 seconds, respectively, along with the variances computed with the microcomputer. These results are summarized in table 9, where one can see that at 214 nm the χ^{2*} statistic is significant at the 97.5% level, the first indication that some precision may accrue from longer integration times. The variances are equivalent according to the χ^{2*} statistic at the other two wavelengths.

To test this further, replicate experiments were run on five solutions in the following manner. The HP8450A was balanced with water in the sample and reference cells. The CoTSPC was placed in the sample cell, thermostatted, and the absorbances measured at 1, 2, 5, 10, 20, and 40 seconds, and repeated five times to give five replicates at each integration time for solution I. After the fifth absorbance measurement, the sample cell was removed, emptied, and refilled with CoTSPC solution. Five replicates were measured at various integration times and the solution was again changed for a total of five solutions. The individual absorbance measurements are recorded in tables 10 through 12; the mean absorbances and variances are collected in table 13; and the two-way ANOVA with replicates at each wavelength is shown in tables 14 through 16.

Table 13 shows that the variances, indeed, are equivalent (χ^2 at 95% level is 11.07 for 5 degrees of freedom) even at 214 nm.

Table 9. Absorbance as a Function of Integration Time for 1.97×10^{-5} M CoTSPC Solution

Integration Times	Absorbance		
	214 nm	321 nm	660 nm
1	1.007 ±9.1[a]	1.074 ±9.1[a]	1.000 ±2.7[a]
2	1.007 ±6.5	1.073 ±6.5	1.001 ±2.5
5	1.007 ±3.9	1.073 ±4.9	1.002 ±2.1
10	1.007 ±6.0	1.072 ±4.9	1.003 ±2.3
20	1.007 ±3.3	1.071 ±3.9	1.004 ±1.6
40	1.008 ±5.5	1.070 ±4.9	1.006 ±1.7
χ^{2*}	14.4	4.5	4.5

[a]Standard deviation computed by spectrophotometer multiplied by 10^4.

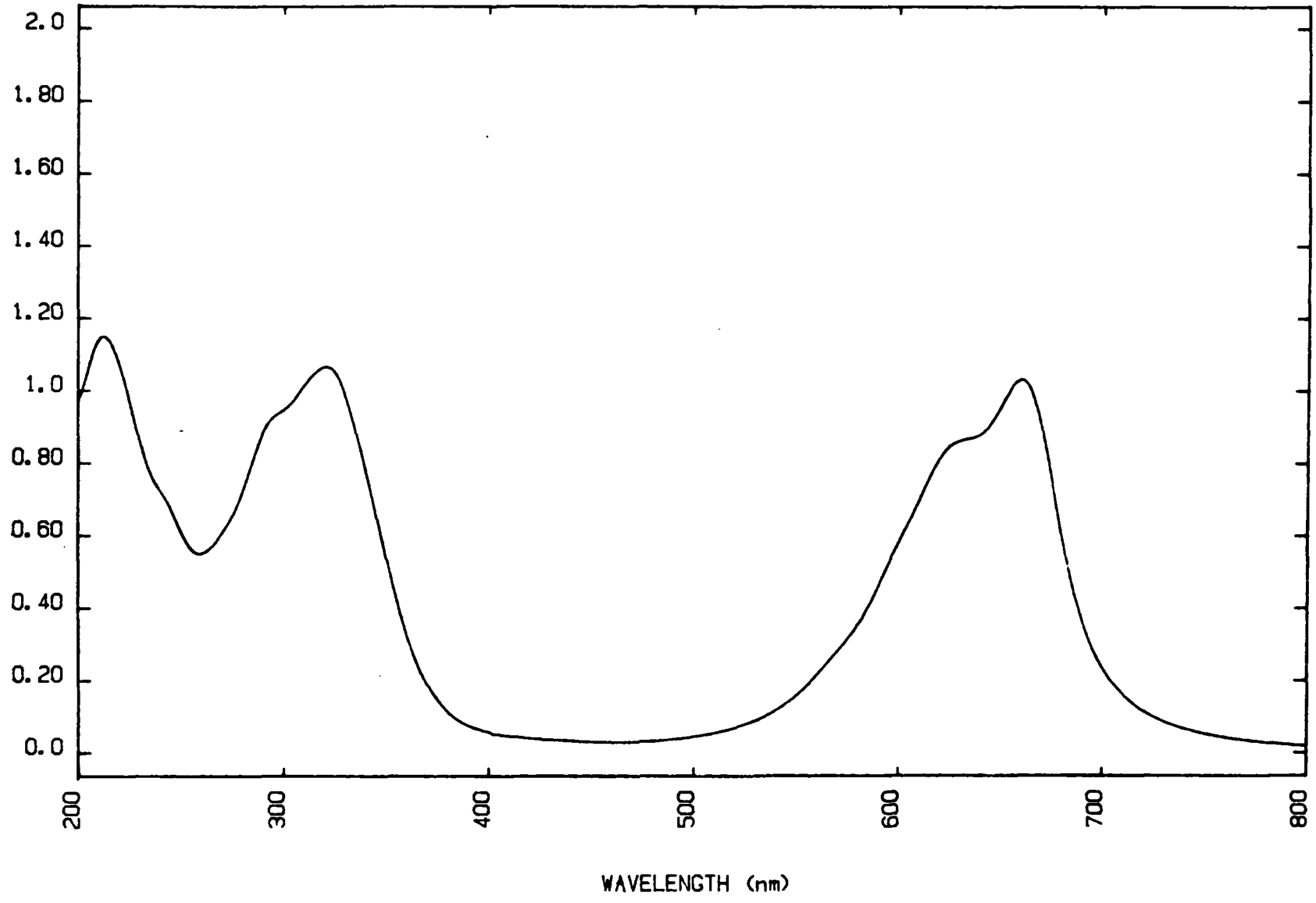

Figure 2. Absorption Spectrum of a 1.97 x 10^{-5} M Solution of CoTSPC in Water at 25° C

Table 10. Absorbance of 1.97×10^{-5} M CoTSPC Solution at 214 nm

Solution	Integration Times					
	1	2	5	10	20	40
I	1.007	1.007	1.007	1.007	1.007	1.008
	1.007	1.009	1.009	1.009	1.008	1.008
	1.009	1.009	1.009	1.009	1.009	1.009
	1.010	1.009	1.011	1.011	1.011	1.012
	1.013	1.011	1.012	1.012	1.013	1.012
II	0.9938	0.9951	0.9945	0.9957	0.9962	0.9954
	.9958	.9947	.9942	.9937	.9942	.9952
	.9941	.9936	.9940	.9938	.9943	.9944
	.9953	.9949	.9943	.9948	.9946	.9944
	.9948	.9955	.9946	.9944	.9944	.9947
III	1.026	1.026	1.026	1.025	1.025	1.025
	1.026	1.027	1.027	1.026	1.025	1.025
	1.025	1.025	1.026	1.026	1.026	1.025
	1.026	1.025	1.025	1.026	1.025	1.025
	1.026	1.026	1.026	1.026	1.026	1.025
IV	1.013	1.008	1.005	1.005	1.007	1.012
	1.011	1.011	1.009	1.006	1.005	1.011
	1.010	1.009	1.008	1.008	1.007	1.008
	1.010	1.008	1.008	1.008	1.008	1.008
	1.010	1.009	1.008	1.008	1.008	1.009
V	1.020	1.019	1.019	1.019	1.019	1.019
	1.020	1.020	1.020	1.019	1.019	1.019
	1.020	1.019	1.020	1.020	1.020	1.020
	1.021	1.019	1.020	1.020	1.020	1.020
	1.022	1.021	1.020	1.021	1.021	1.021

Table 11. Absorbance of 1.97×10^{-5} M CoTSPC Solution at 321 nm

Solution	Integration Times					
	1	2	5	10	20	40
I	1.074	1.073	1.073	1.072	1.071	1.070
	1.073	1.072	1.072	1.071	1.070	1.069
	1.072	1.072	1.071	1.071	1.070	1.070
	1.072	1.072	1.072	1.072	1.071	1.070
	1.070	1.070	1.070	1.069	1.069	1.067
II	1.076	1.076	1.075	1.075	1.073	1.072
	1.074	1.074	1.073	1.073	1.072	1.071
	1.073	1.073	1.073	1.072	1.072	1.070
	1.074	1.073	1.073	1.072	1.071	1.070
	1.072	1.072	1.072	1.072	1.071	1.069
III	1.085	1.085	1.083	1.083	1.082	1.081
	1.083	1.083	1.083	1.083	1.081	1.080
	1.083	1.083	1.083	1.082	1.081	1.080
	1.082	1.082	1.082	1.081	1.081	1.080
	1.081	1.083	1.083	1.082	1.081	1.079
IV	1.081	1.081	1.079	1.078	1.078	1.078
	1.078	1.079	1.079	1.077	1.076	1.077
	1.078	1.078	1.078	1.077	1.076	1.076
	1.078	1.079	1.077	1.077	1.076	1.075
	1.077	1.077	1.077	1.077	1.076	1.075
V	1.087	1.086	1.085	1.084	1.083	1.082
	1.086	1.085	1.084	1.083	1.082	1.081
	1.085	1.085	1.084	1.084	1.083	1.082
	1.083	1.083	1.083	1.083	1.082	1.082
	1.084	1.084	1.083	1.083	1.082	1.081

Table 12. Absorbance of 1.97×10^{-5} M CoTSPC Solution at 660 nm

Solution	Integration Times					
	1	2	5	10	20	40
I	1.000	1.001	1.002	1.003	1.004	1.006
	1.003	1.003	1.003	1.004	1.006	1.007
	1.005	1.004	1.004	1.004	1.004	1.006
	1.002	1.002	1.003	1.004	1.006	1.006
	1.005	1.005	1.005	1.005	1.006	1.008
II	1.006	1.006	1.007	1.008	1.009	1.013
	1.009	1.009	1.009	1.010	1.012	1.015
	1.010	1.009	1.009	1.011	1.013	1.013
	1.012	1.010	1.009	1.010	1.012	1.014
	1.010	1.009	1.010	1.010	1.012	1.014
III	1.004	1.005	1.005	1.007	1.009	1.010
	1.008	1.008	1.008	1.008	1.009	1.011
	1.007	1.007	1.008	1.008	1.010	1.010
	1.008	1.008	1.008	1.008	1.010	1.011
	1.008	1.008	1.010	1.009	1.010	1.012
IV	1.006	1.006	1.007	1.008	1.010	1.011
	1.008	1.008	1.010	1.011	1.011.	1.013
	1.008	1.009	1.008	1.010	1.012	1.014
	1.009	1.009	1.009	1.012	1.013	1.014
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V	1.007	1.006	1.007	1.008	1.010	1.010
	1.006	1.006	1.007	1.007	1.009	1.011
	1.006	1.006	1.006	1.008	1.009	1.010
	1.008	1.008	1.008	1.008	1.010	1.010
	1.007	1.007	1.007	1.009	1.009	1.010

Table 13. Variance of Absorbances Measured for 1.97×10^{-5} M CoTSPC Solution

Integration Times	214 nm		321 nm		660 nm	
	Mean	Variance x 10^6	Mean	Variance x 10^6	Mean	Variance x 10^6
1	1.012	119	1.078	27	1.007	7.4
2	1.012	120	1.078	28	1.007	5.9
5	1.011	125	1.078	26	1.007	5.5
10	1.011	123	1.077	26	1.008	6.0
20	1.011	120	1.076	25	1.010	6.8
40	1.012	113	1.075	27	1.011	7.8
χ^{2*}		0.07		0.10		1.1

Table 14. ANOVA Table for 1.97×10^{-5} M CoTSPC at 214 nm

Source	TSS[a]	MS	df	F
Solution	17,075.40	4269	4	2,837[b]
Integration Time	17.23	3.4	5	2.3
Interaction	52.03	2.6	20	1.7
Error	180.58	1.5	120	
Total	17,325.25			

[a]Numbers coded by absorbance x 10^3-990

[b]Significant at 99% level (F(4,20) = 4.43)

Table 15. ANOVA Table for 1.97×10^{-5} M CoTSPC at 321 nm

Source	TSS[a]	MS	df	F
Solution	3,667.51	916.88	4	752[b]
Integration Time	174.16	34.88	5	29[b]
Interaction	6.57	0.33	20	0.3
Error	146.40	1.22	120	
Total	3,994.64			

[a]Numbers coded by absorbance x 10^3-1,000

[b]Significant at 99% level ($F(5,20) = 4.10$)

Table 16. ANOVA Table for 1.97×10^{-5} M CoTSPC at 660 nm

Source	TSS[a]	MS	df	F
Solution	734.49	183.62	4	114[b]
Integration Time	362.53	72.51	5	45[b]
Interaction	16.07	0.80	20	0.5
Error	193.20	1.61	120	
Total	1,306.29			

[a]Numbers coded by absorbance x 10^3-1,000

[b]Significant at 99% level

Table 17 attempts to summarize the results from the previous tables by listing the F-ratios from the ANOVA and the mean value of the variances computed by the microcomputer over all the integration times. One can see that removing and refilling the sample cell introduce a significant error at all wavelengths. At two wavelengths (321 nm and 660 nm), the variance among mean values over the integration times is significantly greater than the residual variance, which implies that the mean absorbances from the various integration times are significantly different. As with the holmium oxide, one notes that the variance computed with the microcomputer underestimates the variance from replicates (the residual variance in the ANOVA). The final point is that the residual variance is the same at each wavelength, while the total error is significantly greater at 214 nm than at 321 and 660 nm, suggesting that the far UV region is more susceptible to error when the sample cell is removed and refilled.

The next stage in the analysis was to contrast various combinations of the mean absorbances at 321 and 660 nm. For this we will use the Q statistic,[8] defined as

$$Q = \frac{q(k,\nu)\cdot S}{\sqrt{N}} \qquad (2)$$

where $q(k,\nu)$ = test statistic where k is number of groups and ν is degrees of freedom,

S = within-group standard deviation, and

N = number of observations in each group.

For the situation under discussion here, k = 6 (number of integration times), ν = 120, and N = 25. At the 99% confidence level $q(6,120) = 4.71$.[8] Using the residual standard deviations, one can compute the Q statistic and test the null hypothesis that the means computed at various integration times are from the same population.[8] The results of these comparisons are shown in tables 18 and 19. In both cases, the mean absorbances for 1, 2, 5, and 10 satisfy the null hypothesis that they are all from the same population, while the means at 20 and 40 seconds integration time are significantly different. Thomas[2] remarked in his analysis of the HP8450A that the dark current began to drift after 10 seconds, so it is possible, then, that using integration times exceeding 10 seconds not only fails to decrease the variance, but also introduces a systematic error in the mean value of the measured absorbance.

Table 17. Summary of Two-Way ANOVA for 1.97×10^{-5} M CoTSPC

Source	F-Ratio		
	214 nm	321 nm	660 nm
Row (Solution)	2,837[a]	752[a]	114[a]
Column (Integration time)	2.3	29[a]	45[a]
Interaction	1.7	0.3	0.5
Residual variance x 10^6	1.5	1.2	1.6
Total variance x 10^6	116	26.8	8.8
Mean variance computed by spectrophotometer x 10^6	0.32	0.32	0.048
Ratio residual to computed variances	4.7	3.8	33

[a]Significant at 99% level

Table 18. Comparison of Means from Various Integration Times - 321 nm

Integration times	1	2	5	10	20	40	Q statistic = 1.0[a]
Mean absorbance	1.078	1.078	1.078	1.077	1.076	1.075	
	1/5	1/5	1/5	1/5	1/5	-1	1.6
	1/4	1/4	1/4	1/4	-1	0	1.8
	1/3	1/3	1/3	-1	0	0	1.0

[a] $q(6.120) = 4.71$ at 99% level, $S^2 = 1.2$, N = 25.

Table 19. Comparison of Means for Various Integration Times - 660 nm

Integration Times	1	2	5	10	20	40	Q statistic = 1.2[a]
Mean Absorbance	1.007	1.007	1.007	1.008	1.010	1.011	
	1/5	1/5	1/5	1/5	1/5	-1	4.2
	1/4	1/4	1/4	1/4	-1	0	2.8
	1/3	1/3	1/3	-1	0	0	1.0

[a] $q(6.120) = 4.71$ at 99% level, $S^2 = 1.6$, N = 25.

3.3 Diluted CoTSPC Solution.

Figure 3 illustrates the absorption spectrum for the diluted CoTSPC solution such that the peak absorbances are in the neighborhood of 0.01 absorbance units at 25° C. The peaks at 321 and 660 nm shift to 324 and 662 nm as more monomeric CoTSPC is formed at the lower concentration.

The same experiments were run for the diluted CoTSPC solution and the results recorded in tables 20 through 29.

Table 20 shows that the variances computed with the spectrophotometer's microcomputer are equivalent for each integration time. In table 24 the variances from replicate measurements at each integration time are also seen to be equivalent.

Table 28 summarizes the F-ratios from the ANOVA tables at each wavelength. In accord with the results for the standard CoTSPC solution, the removal of the sample cell to refill it with a new solution introduces a significant error. For the dilute solution, only at one wavelength, 324 nm, does the variance of the mean absorbances over the integration times differ significantly from t' residual variance. The contrast among means in table 29 shows that the e or

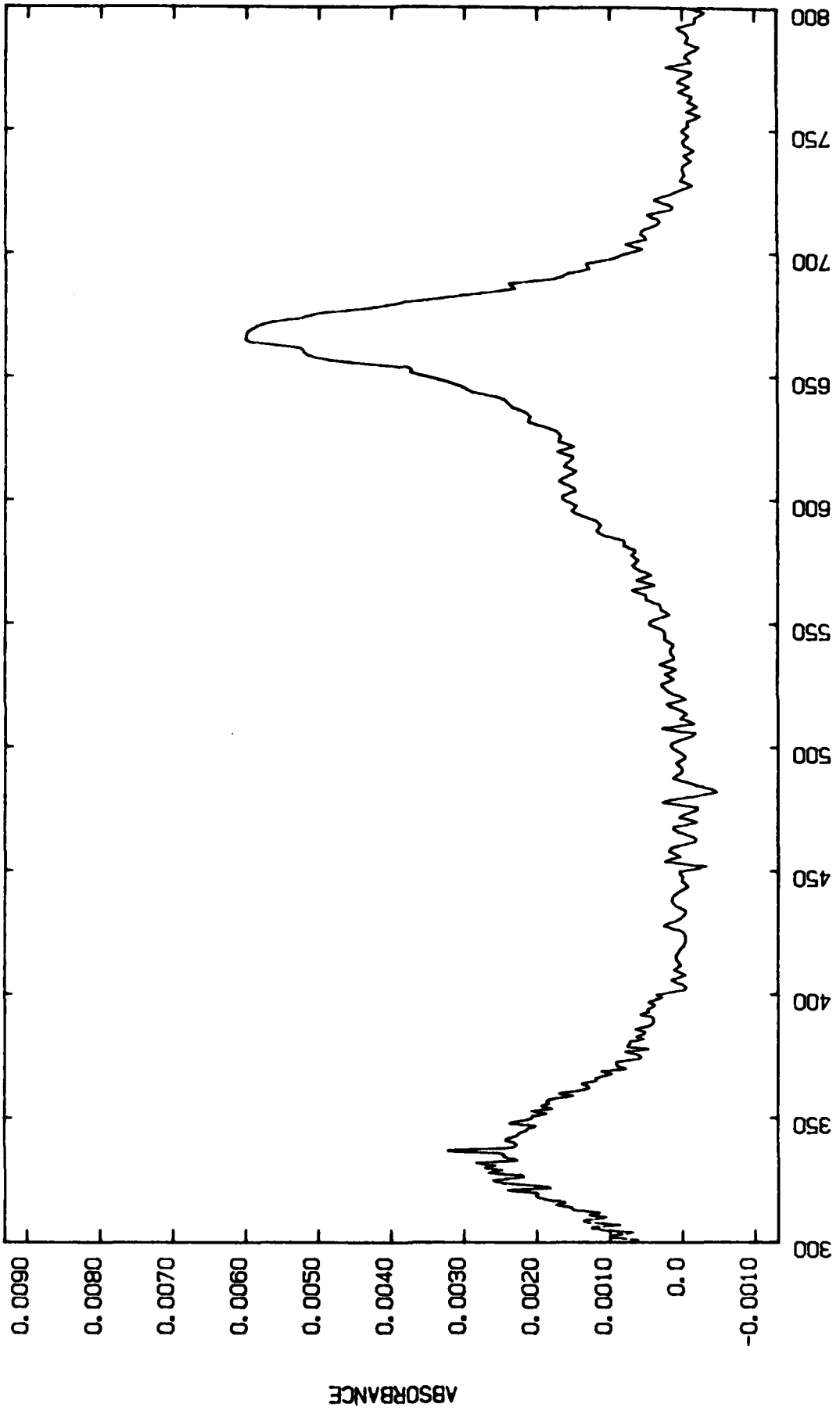

Figure 3. Absorption Spectrum for the Diluted CoTSPC Solution such that the Peak Absorbances are in the Neighborhood of 0.01 Absorbance Units at 25° C.

is caused by the inclusion of the mean at the shortest integration time of 1 second. For such dilute solutions, it might be prudent to use a 2-second or longer integration time if possible. Finally, one sees again that computed variances underestimate the residual variances. Table 30 compares variances of the standard and the dilute CoTSPC solutions, showing that the variance is the same at all wavelengths, and significantly less for the dilute solution.

One of the major conclusions from these experiments is that, in order to get the maximum precision available from the HP8450A, one should not remove the sample cell to refill it. Thus, the use of flow cells for analyses such as James[3] reproted on multicomponent metal analysis are a necessity for high-precision work. To confirm this, the spectrum of the standard CoTSPC solution was determined with a flow cell. A solution was placed in the cell and five replicates measured with a one-second integration time after which the cell was flushed and the experiment repeated. For an unknown reason, the flow cell interfered with measurements in the visible region, so a standard 1-cm cell was emptied with a tube attached to a trap leading to a vacuum line. Again five replicate measurements were made at 660 nm, after which the sample cell was flushed four times, then refilled, and the experiment repeated. Table 31 lists these results. In Table 32, the standard deviations with the flow cell are compared with the residual standard deviations and total standard deviations recorded when the sample cell was removed, cleaned, and refilled. At all wavelengths, the flow cell reduces the error compared to removing the cell; at 660 nm one sees that the error is even less than the residual standard deviation, confirming the need to leave the sample cell in the instrument for high-precision analysis.

Table 20. Absorbance as a Function of Integration Time for Diluted CoTSPC Solution

Integration Times	Absorbance		
	214 nm	324 nm	662 nm
1	0.0097 ±0.97[a]	0.0090 ±1.6[a]	0.0105 ±0.97[a]
2	.0097 ±2.1	.0092 ±1.7	.0105 ± .87
5	.0098 ±1.5	.0090 ±1.6	.0106 ± .68
10	.0099 ±1.1	.0091 ±1.2	.0108 ± .81
20	.0099 ±1.1	.0091 ±0.97	.0106 ± .57
40	.0107 ±0.97	.0091 ±1.1	.0106 ± .61
χ^{2*}	7.7	5.7	4.6

[a]Standard deviation computed by spectrophotometer multiplied by 10^4

Table 21. Absorbance of Diluted CoTSPC Solution at 214 nm

Solution	Integration Times					
	1	2	5	10	20	40
I	0.00974	0.0097	.0098	.0099	0.00990	0.01070
	.0108	.0105	.0107	.0105	.01062	.01109
	.0114	.0116	.0114	.0115	.01141	.01156
	.0119	.0117	.0118	.0116	.0118	.01193
	.0127	.0118	.0120	.0121	.0120	.01218
II	0.0158	0.0136	0.0127	0.0124	0.0124	0.01297
	.0131	.0129	.0130	.0136	.0132	.01292
	.0138	.0136	.0135	.0133	.0134	.0135
	.0147	.0148	.0148	.0150	.0149	.01435
	.0147	.0147	.0148	.0148	.0147	.0145
III	0.0122	0.0106	0.0106	0.0117	0.0091	0.00860
	.0095	.0099	.0096	.0095	.0096	.00948
	.0100	.0102	.0103	.0103	.0104	.01010
	.0101	.0102	.0101	.0101	.0100	.00993
	.0104	.0105	.0105	.0103	.0103	.01010
IV	0.00699	0.0071	0.0073	0.0070	0.0067	0.0066
	.0069	.0067	.0071	.0070	.0071	.0067
	.0067	.0067	.0065	.0064	.0067	.0066
	.0064	.0062	.0063	.0063	.0063	.0064
	.0067	.0066	.0065	.0062	.0062	.0063
V	0.0093	0.0092	0.0091	0.0087	0.00890	0.00919
	.0092	.0093	.0092	.0089	.00840	.00817
	.0087	.0089	.0087	.0085	.00840	.00848
	.0083	.0079	.0082	.0079	.00795	.00812
	.0086	.0084	.0082	.0082	.00798	.00740

Table 22. Absorbance of Diluted CoTSPC Solution at 324 nm

Solution	Integration Times					
	1	2	5	10	20	40
I	0.0090	0.0092	0.0090	0.0091	0.0091	0.0091
	.0094	.0090	.0091	.0089	.00887	.0090
	.0089	.0090	.0088	.0089	.0089	.00888
	.0092	.0087	.0089	.0087	.0089	.0088
	.0097	.0089	.0086	.0087	.0087	.00872
II	0.0087	0.0089	0.0087	0.0085	0.0084	0.00851
	.0088	.0085	.0085	.0090	.00854	.0084
	.0091	.0083	.0085	.0084	.0084	.0085
	.0091	.0091	.0086	.0084	.0085	.0082
	.0085	.0083	.0085	.0084	.0085	.0082
III	0.0098	0.0092	0.0089	0.0092	0.0090	0.0090
	.0090	.0092	.0088	.0089	.0088	.00871
	.0086	.0087	.0088	.0090	.0088	.00874
	.0088	.0087	.0087	.0087	.0085	.0084
	.0089	.0088	.0087	.0085	.0086	.0085
IV	0.0088	0.0090	0.0089	0.0087	0.0087	0.0086
	.0090	.0086	.0088	.0088	,0088	.00858
	.0085	.0088	.0087	.0086	.0087	.0086
	.0087	.0087	.0085	.0086	.0085	.00864
	.0090	.0087	.0086	.0085	.0086	.00842
V	0.0093	0.0094	0.0092	0.0092	0.0094	0.00922
	.0096	.0091	.0093	.0091	.0090	.0090
	.0092	.0093	.0091	.0089	.0089	.0088
	.0092	.0090	.0090	.0088	.0089	.00869
	.0090	.0084	.0087	.0089	.0087	.0087

Table 23. Absorbance of Diluted CoTSPC Solution at 662 nm

Solution	Integration Times					
	1	2	5	10	20	40
I	0.01047	0.01052	0.01060	0.01084	0.01063	0.01057
	.01072	.01077	.01073	.01032	.01043	.01055
	.01060	.01049	.01033	.01054	.01044	.01045
	.01040	.01050	.01041	.01016	.01054	.01041
	.01042	.01052	.01024	.01038	.01044	.01044
II	0.01010	0.01010	0.01031	0.01034	0.01042	0.01033
	.01023	.01005	.01020	.01076	.01027	.01031
	.01010	.01010	.01028	.01009	.01025	.01016
	.01001	.01030	.01034	.01038	.01051	.01025
	.01009	.01028	.01022	.01019	.01066	.01022
III	0.01147	0.01141	0.01147	0.01169	0.01130	0.01157
	.01125	.01125	.01131	.01125	.01125	.01122
	.01138	.01174	.01097	.01137	.01104	.01120
	.01122	.01123	.01113	.01100	.01094	.01110
	.01070	.01088	.01125	.01096	.01117	.01092
IV	0.01196	0.01116	0.01167	0.01149	0.01138	0.01147
	.01173	.01175	.01183	.01172	.01150	.01143
	.01115	.01142	.01138	.01148	.01150	.01158
	.01141	.01152	.01170	.01143	.01131	.01144
	.01113	.01124	.01159	.01136	.01141	.01128
V	0.01208	0.01201	0.01214	0.01212	0.01219	0.01204
	.01186	.01189	.01183	.01182	.01169	.01195
	.01181	.01162	.01169	.01157	.01160	.01154
	.01160	.01173	.01179	.01170	.01158	.01141
	.01114	.01150	.01141	.01148	.01158	.01153

Table 24. Variance of Absorbances for Diluted CoTSPC Solution as Computed by Microcomputer in the HP8450A

Integration Times	214 nm		324 nm		662 nm	
	Mean	Variance x 10^8	Mean	Variance x 10^8	Mean	Variance x 10^8
1	0.0103	750	0.0090	11.8	0.0110	43
2	.0101	640	.0088	9.3	.0110	39
5	.0101	620	.0088	5.1	.0111	41
10	.0101	680	.0088	6.2	.0111	38
20	.0099	650	.0088	5.7	.0110	29
40	.0099	670	.0087	6.9	.0110	35
χ^{2*}		0.25		6.2		1.2

Table 25. ANOVA Table for Diluted CoTSPC at 214 nm[a]

Source	TSS	MS	df	F
Solution	89,629.68	22,407.42	4	444[b]
Integration Time	306.55	61.31	5	1.21
Interaction	355.98	17.80	20	0.35
Error	6,058.08	50.48	120	
Total	96,350.29			

[a]Numbers coded by absorbance x 10^4

[b]Significant at 99% level

Table 26. ANOVA Table for Diluted CoTSPC at 324 nm[a]

Source	TSS	MS	df	F
Solution	434.0	108.5	4	21.15[b]
Integration Time	189.93	36.99	5	7.21[b]
Interaction	30.53	1.53	20	0.30
Error	615.62	5.13	120	
Total	1,265.08			

[a]Absorbance x 10^4

[b]Significant at 99% level

Table 27. ANOVA Table for Diluted CoTSPC at 662 nm[a]

Source	TSS	MS	df	F
Solution	4,816.83	1,204.21	4	265[b]
Integration Time	8.75	1.75	5	0.39
Interaction	53.36	2.77	20	0.61
Error	544.96	4.54	120	
Total	5,425.90			

[a]Absorbance x 10^4

[b]Significant at 99% level

Table 28. Summary of F-Ratios from Two-Way ANOVA for Diluted CoTSPC Solution

	214 nm	324 nm	662 nm
Row (solution)	444[a]	21[a]	265[a]
Column (integration time)	1.2	7.2[a]	0.39
Interaction	0.35	0.3	0.61
Residual variance x 10^8	51	5.1	4.5
Total variance x 10^8	647	8.5	36.4
Mean variance computed by spectrophotometer x 10^8	1.7	2.0	0.56
Ratio residual to mean computed variance	30	2.6	8.0

[a]Significant at 99% level

Table 29. Comparison of Means from Various Integration Times - 324 nm

Integration times	1	2	5	10	20	40	Q Statistic = 1.75
Mean absorbance	0.0090	0.0089	0.0088	0.0088	0.0087	0.0087	
	-1	1/5	1/5	1/5	1/5	1/5	2.2
	0	-1	1/4	1/4	1/4	1/4	1.25

Table 30. Comparison of Residual Variances for 1.97 x 10^{-5} M CoTSPC with Diluted Solution

	Wavelength (nm)					
	214	214	321	324	660	662
Residual variance x 10^8	150	51	120	5.1	160	4.5
Ratio		2.9[a]		24[a]		36[a]

[a]F(120,120) = 1.53 at 99% confidence level.

Table 31. Absorbance Measurements with Flow Cell

	λ = 214 nm	λ = 324 nm	λ = 660 nm
I	1.153	1.073	1.020
	1.152	1.071	1.021
	1.151	1.069	1.020
	1.148	1.072	1.022
	1.154	1.070	1.022
II	1.148	1.076	1.022
	1.146	1.072	1.022
	1.149	1.073	1.022
	1.150	1.076	1.022
	1.146	1.077	1.023
III	1.146	1.078	1.021
	1.152	1.077	1.021
	1.146	1.075	1.021
	1.148	1.074	1.021
	1.145	1.075	1.021
IV	1.145	1.075	---
	1.147	1.077	---
	1.146	1.068	---
	1.153	1.076	---
	1.150	1.073	---
V	1.147	1.074	---
	1.152	1.074	---
	1.148	1.074	---
	1.147	1.073	---
	1.148	1.073	---

Table 32. Summary of Absorbance Measurements in Flow Cell

	Wavelength, nm		
	214	321	660
Std Dev, flow cell x 10^3	2.8	2.6	0.8
Std Dev, residual x 10^3	1.2	1.1	1.3
Total Std Dev x 10^3	10.8	5.2	3.0
Ratio of variances (total/flow cell)	15	4	14
Ratio of variances (flow cell/residual)	5.4	5.6	0.4

4. CONCLUSIONS

Two major conclusions arose from these experiments. First, the precision of absorbances measured at integration times was equivalent. Second, it was shown that a significant error is introduced when the sample cell is removed from the cell compartment for refilling. To achieve the maximum precision sensitivity available from the instrument, the sample cell should be left in the cell compartment between refills, and spectra of standards should be run at the same time as unknowns.

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APPENDIX

THEORY OF OPERATION OF THE HP8450A AS DESCRIBED IN OPERATOR's HANDBOOK

The basis of the measurement process is the electronic response of each photodiode in the detector arrays. This produces a signal for each diode which is linearly related to the amount of light at the corresponding wavelength transmitted by the substance being measured. Since in the absence of light the diode arrays do not produce signals of zero, a measurement of the signals at zero light, referred to as a dark current, D, must be made and used to correct the transmittance measurement to produce a value which is directly proportional to the transmittance of the substance being measured.

When measurements are made on substances placed in a light path designated for "samples", they are always referenced to measurements made virtually simultaneously on substances placed in the light path designated for "reference". This eliminates contributions to the final result from sources such as lamp intensity fluctuation. However, because the "sample" and "reference" light paths are physically different, having different reflecting surfaces, different containers (cells) for the substances being measured, etc., the amount of light transmitted and/or measured at each wavelength may not be the same for all paths. To avoid having these differences contribute to the spectrum measured for a sample it is necessary for a "balance" measurement to be made. The difference in light paths found in this "balance" measurement are stored by the HP8450 and used to correct subsequent measurements.

Balance

To make a balance measurement, the sample and reference cells are filled with the chosen solvent and the operation MEASURE BALANCE EXECUTE is initiated. This causes the following:

1. The radiant energy is directed through the sample path and the sample balance current, S_b of each diode is measured.

2. The radiant energy is directed through the reference path and the reference balance current, R_b, of each diode is measured.

3. The radiant energy to the photodiode array is effectively turned-off and the dark current, D, of each of the 401 diodes is measured.

4. The balance spectrum to be used to correct subsequent measurements is calculated from the relation:

$$\text{BALANCE} = -\log \frac{(S_b - D)}{(R_b - D)} \qquad \text{A - (1)}$$

Measurement

To make a measurement the sample cell is filled with a mixture of the solvent and the solute whose absorbance is to be measured and placed in the sample path. After this is done, the user initiates the operation MEASURE ABSORBANCE EXECUTE. When EXECUTE is pressed the HP 8450 performs the following operations:

1. The radiant energy is directed through the sample cell and the sample measure current, S_m, of each diode is measured.

2. The radiant energy is directed through the reference cell and the reference measure current, R_m, of each diode is measured.

3. The dark current, D, is measured and its running average updated.

4. The result is calculated from the relation:

$$\text{RESULT} = -\log \left[(S_m - D)/(R_m - D)\right] - \text{BALANCE} \qquad \text{A - (2)}$$

$$= -\log (S_m - D) + \log (R_m - D) + \log (S_b - D) - \log (R_b - D)$$

Result

Now it will be shown that if one condition is met, this result is the absorbance of the solute in the sample cell. The condition is that the diode current, C, be proportional to the radiant energy, E, that is transmitted through the cell of C = K E+D where K is the proportionality constant. The relation between the radiant energy incident on the cell, I, and the transmitted energy, E, is:

$$E = (T_{cell}) \times (T_{contents}) \times (I)$$

where T_{cell} is the transmittance of the cell alone and $T_{contents}$ is the transmittance of the contents of the cell.

Substituting this relation for E into the expression for diode current and taking the logarithm gives:

$$\log (C - D) = \log (KI) = \log (T_{cell}) = \log (T_{contents}) \qquad \text{A - (3)}$$

$$= \log (KI) - A_{cell} - A_{contents}$$

where A, the absorbance, is defined as -log T.

The four currents in equation (2) can be related to the absorbances in equations (3) as follows, where S and s and R and r denote sample and reference respectively:

$$\log (S_m - D) = \log KI_s - A_s(\text{solvent}) - A_s(\text{solute}) - A_s(\text{cell}) \quad \text{A-(4)}$$

$$\log (R_m - D) = \log KI_r - A_r(\text{solvent}) - A_r(\text{cell}) \quad \text{A-(5)}$$

$$\log (S_b - D) = \log KI_s - A_s(\text{solvent}) - A_s(\text{cell}) \quad \text{A-(6)}$$

$$\log (R_b - D) = \log KI_r - A_r(\text{solvent}) - A_r(\text{cell}) \quad \text{A-(7)}$$

If equations (4) through (7) are substituted into (2), it can be shown that the result of the measurement in the HP 8450 is the absorbance of the solute in the sample cell or,

$$\text{RESULT} = A_s(\text{solute}) = \text{absorbance of sample solute} \quad \text{A-(8)}$$

Measurement Errors

To obtain greater accuracy, the HP 8450 makes several measurements of the current of each photodiode and then estimates mean values. The uncertainty associated with the estimate of the mean is calculated also. This estimated error is carried through to all future calculations so that the user knows how much confidence to place in each result. In this section the way in which the estimate of the error is calculated is described and an example of how to use the error information is given.

Whenever a measurement is to be made, the beam is directed to one of the five positions and the current of each diode is measured N times. The value of N depends upon the integration time that is specified by the user and is shown in the table below. If the specified integration time is greater than 1.7 seconds, the number of measurements N, is determined by repeated one second measurements until the remainder is less than 1.7 seconds and then the remaining measurements are made per the table. For example, if the specified integration time is 5.6 seconds, there would be four one-second blocks followed by a 1.6 second block and N would be (4 x 2) + 3 = 11.

Integration Time	Measurements
1.0	2
1.2	3
1.7	4
2.2	5

When the HP 8450 is idle, the dark current of each photodiode is measured several times and an average dark current is calculated for greater accuracy. Dark currents are also measured between the other measurements.

After each diode current has been measured, the average dark current is subtracted from each measured value. The i th dark current corrected value will be represented by the symbol I_i. It corresponds to the values $R_b - D$, $R_m - D$, $S_b - D$, and $S_m - D$ described on pages 7-11. Next, an estimate of the mean dark corrected diode current, $\bar{I}$, and a number expressing the uncertainty associated with the estimate will be calculated. The uncertainty is called the estimated error of the mean and is represented by the symbol $\sigma_{\bar{I}}$.

The estimate of the mean dark corrected current is given by

$$\bar{I} = \frac{\sum_{i=1}^{N} I_i}{N} = \left[\frac{\sum_{i=2}^{N} (I_i - I_1)}{N}\right] + I_1 \qquad \text{A-(9)}$$

The second form is used in the actual calculation because the numbers are smaller and register overflow is not a problem.
The estimated error of the mean is approximately

$$\sigma_{\bar{I}} = \sqrt{\frac{\sigma_s^2}{N}} \qquad \text{A-(10)}$$

where σ_s is the sample standard deviation given by

$$\sigma_s = \sqrt{\frac{\sum_{i=1}^{N} (I_i - \bar{I})^2}{N - 1}} \qquad \text{A-(11)}$$

When equation (3) is substituted into equation (2) an expression for the estimated error of the calculated mean is

$$\sigma_{\bar{I}} = \sqrt{\frac{\sum_{i=1}^{N} (I_i - \bar{I})^2}{N(N - 1)}} \qquad \text{A-(12)}$$

This value is carried through all the future calculations using all necessary propagation of error adjustments. It is displayed on the CRT following the sigma symbol or printed following the symbol s.

As an example, in the equation RESULT = -log $(S_m - D)$ + log $(R_m - D)$ + log $(S_b - D)$ - log $(R_b - D)$, if the estimated error in $S_m - D$ is σ_{sm}, the estimated error in $R_m - D$ is σ_{rm}, the estimated error in $S_b - D$ is σ_{sb}, and the estimated error in $R_b - D$ is σ_{rb}, then the estimated standard deviation of the result is

$$\sigma_{\bar{I}} = \sqrt{\frac{\sigma_{sm}^2}{(S_m - D)^2} + \frac{\sigma_{rm}^2}{(R_m - D)^2} + \frac{\sigma_{sb}^2}{(S_b - D)^2} + \frac{\sigma_{rb}^2}{(R_b - D)^2}} \qquad \text{A-(13)}$$

END

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